



Application of solid phase extraction procedures for rare earth elements determination in environmental samples



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ABSTRACT

Determination of rare earth elements in environmental samples requires often pre-concentration and separation step due to a low metal content and high concentration of the interfering matrix components. A solid phase extraction technique with different kind of solid sorbents offers a high enrichment factor, rapid phase separation and the possibility of its combination with various detection techniques used either in on-line or off-line mode. The recent developments in this area published over the last five years are presented and discussed in this paper.

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1. Introduction

The rare earth elements (REEs) or rare earth metals (REMs) as defined by IUPAC, represent a group of 17 transient metals. They comprise scandium, yttrium and further 15 elements called lanthanides, ranging from the most abundant cerium and lanthanum to the less frequent lutetium. The natural abundances of REEs greater than their name would suggest, with several elements being present at an average content of 30 mg kg⁻¹ on the Earth's crust [1]. They exhibit similar physical and chemical properties,

including low solubility and immobility in the terrestrial crust, and are generally in the +3 valence state over a wide range of oxygen fugacity (with Eu²⁺ and Ce⁴⁺ exception). Their ionic radii decrease with an increase of atomic number from 103 pm in La³⁺ to 0.86 pm in Lu³⁺ (phenomenon known as “lanthanide contraction”). One of the lanthanides, promethium, is radioactive and usually sourced through nuclear transformations.

Rare earth elements and their compounds, due to the unique magnetic, electric and optical properties, are used in many kinds of industrial products, such as the photo luminescence materials, magnetic alloys, catalysts for petroleum refining, carrier materials of automobile exhaust catalysts and high-refractive index low-dispersion optical glasses. The gadolinium compounds are also

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used in medicine as magnetic resonance imaging contrast reagents [2]. Moreover, LaCl_3 is added to the chemical fertilizers in China to increase the yields of crop [3]. Due to their chemical similarity and high weather-resistance, the concentrations of rare earths in rocks are only slowly changed by geochemical processes, making the distribution of the relative abundances of REEs very useful for geochronology and may also yield important geochemical information and assists in the understanding of the processes occurring in seawater [4,5].

Since the use of REEs in industrial applications has been increased growing, the possibility of their release into the environment has also increased. The anthropogenic input, combined with low natural background of REEs, have the potential to influence their distribution pattern, particularly in estuarine and coastal waters [6]. Additionally, there is a growing concern about the potential toxicity of gadolinium to the living organisms, due to its influence on the biochemistry of calcium and associated cellular processes [7]. Thus, the accurate and precise analytical methods are needed for their determination in various samples [8]. Neutron activation analysis (NAA) [9], X-ray fluorescence spectrometry (XRF) [10], inductively coupled plasma optical emission spectrometry (ICP OES) [11] and inductively coupled plasma mass spectrometry (ICP MS) [12–14] are the most frequently employed analytical techniques for the determination of REEs. NAA, requires a nuclear reactor, which is not commonly available as well as sample preparation is tedious. ICP OES has the capability for multi-element detection, however, the content of REEs is usually lower than the limit of detection of this technique and matrix components may cause some interferences. ICP MS has become one of the most powerful technique for determination of REEs owing to its low detection limits, wide linear dynamic range and its capability to perform multi-element and isotopic analysis. The instrumental methods for determination of REE have been recently reviewed [8,15]. However, the direct determination of REEs in seawater samples with ICP MS is still a challenge due to the remarkable matrix effect and potential spectral interferences (isobaric and polyatomic). A high salt content in seawater causes instrument sensitivity drift, signal suppression and clogging of the sample introduction and ions extraction systems. On the other hand, in many environmental samples some coexisting elements such as barium, tin and antimony possibly bring serious spectral interference (oxides ions and hydroxides) during the ICP MS determination of europium, lanthanum and cerium.

Therefore, to solve these problems and render more sensitive, accurate and interference-free determination, an enrichment step usually precedes the measurements. Among different separation and pre-concentration techniques, batch and column approaches in which REEs are sorbed on different water-insoluble solid materials and further eluted with acids or complexing reagents have been widely used. The solid phase extraction (SPE) procedures offer a number of important advantages in comparison with classical liquid-liquid extraction, such as reduced organic solvents usage and exposure, high enrichment factor, rapid phase separation and the possibility of combination with different detection techniques [16]. The broad range of sorbent materials along with the various chelating reagents and eluents make this technique very attractive for sample pretreatment. Moreover, they can be easily implemented and controlled in flow systems to perform appropriate sample pretreatment. The mechanism of sorption depends on the nature of a given sorbent and may include simple adsorption, complexation or ion-exchange. The choice of solid material for enrichment and removal of REEs should be based on the content of the analyte, sample matrix and technique used for final detection, whereas higher enrichment factors can be obtained under adequate experimental conditions (a time of sample loading, a sorbent mass, a volume of eluent).

The purpose of this paper is to present and discuss some of the recent developments and tendencies on the research related to the separation and preconcentration techniques used for REEs determination in the environmental samples. The period reviewed here includes the publications that appeared since 2010 up to 2015. Some earlier citations illustrate a specific point. More details regarding earlier contributions can be found in the review papers [8,17,18].

2. Approaches for solid phase extraction

From the methodological standpoint, two basic approaches can be recognized in SPE, on-line and off-line procedures. In off-line preconcentration/separation mode, the enriched phase is manually transferred to the detector. On-line approach enables high sample throughput with lower sample contamination as all operations are carried out automatically.

2.1. Off-line mode

In the classical SPE, an appropriate sorbent is packed in a column, followed by loading the liquid sample to retain an analyte and then elution step is performed. Modern trends in SPE, except the development of novel sorptive materials, are toward simplification, miniaturization and low consumption of organic solvents and samples [19].

Stir bare sorptive extraction (SBSE) has an extraction mechanism similar to that of solid phase microextraction (SPME), but uses much larger extraction volume, resulting in higher absorption capacity, higher recoveries and solvent-free nature [20]. However, there are some problems associated with SBSE, such as limitation in commercial coating and coating abrasion of laboratory-made stir bar. Several studies aimed at elaborating either novel materials used for coating magnetic stirrers or new variants of SBSE are continuously being conducted, which were summarized in the recent reviews [19,21].

One of the variations of the solid phase technique which considerably reduces the time and simplifies the extraction is dispersive SPE, in which extraction is not carried out in the column, cartridge or disk but is dispersed in the liquid sample. Compared with classic SPE methods, preconditioning of the sorbent is not necessary, simplifying its performance and reducing the extraction time. Several nanomaterials have been investigated as solid phase sorbents for this technique, such as carbon nanotubes, graphene oxide and molecularly imprinted nanoparticles [22–24]. Particularly, nanoparticles contain magnetic components allow convenient and highly efficient enrichment. In this procedure, nanoparticles are dispersed into the sample solution, and after adsorption process they are easily separated from the matrix by applying an external magnet while the solution is discarded. Then, the target analytes are desorbed with a suitable solution and nanoparticles are regenerated for reusing as it is shown schematically in Fig. 1.

2.2. On-line mode

Flow systems, where the aqueous sample is introduced into the analytical path and processed inside it under reproducible conditions, have proved to be excellent tools for automation of sample pretreatment with on-line separation and/or preconcentration techniques based on sorption principles. Briefly, flow injection analysis (FIA) is based on a injection of a precise sample volume into a moving carrier or reagent stream. In the course of its travel through the reaction coil, the sample zone disperses and reacts with the reagent to form a detectable species [25]. As opposed to

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